[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Induction Period in Gaseous Thermal Explosions[1]

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We have recently studied the explosions of azomethane[2a] and ethyl azide,[2b] and have shown that they are probably thermal explosions, due to self-heating of the gas on account of the exothermicity of their slow decompositions. In these papers we have compared our results with the theory of Semenoff,[3] which gives the critical explosion pressure as a function of the temperature. Now it is observed when the gases are admitted to the reaction vessel that an appreciable time elapses before the explosion occurs. These lag times or induction periods have been measured in many cases, and in this paper we shall present these data, and discuss the theory. We shall see that this enables us to make an estimate of the heat of decomposition.

The basis of the theory which we shall present consists in following the change of temperature of the gas as reaction proceeds. An equation giving the amount, T, by which the temperature of the reacting gas exceeds that of its container as a function of the time and from which the induction period can be obtained has been given by Allen and Rice.[2a] The rate of production of heat is given by the expression $QknV$, where Q is the heat of reaction per mole of gas decomposed, V the volume of the reaction vessel, n the number of moles of reacting gas per unit volume, and k the rate constant. $k = Ae^{-E/R(T + T_0)}$, A being a constant, R the gas constant, E the activation energy for the unimolecular decomposition, and $T + T_0$ the temperature of the gas; T_0 is the temperature of the reaction vessel. We may write $n = n_0e^{-kT}$, where n_0 is the initial value of n and t is the time, provided we assume as an approximation that k is constant during the induction period. Heat is removed from the gas by conduction and convection at the rate axT, a being the wall area and x a constant. Subtracting the rate of loss of heat from the rate of production and dividing by C, the total heat capacity of the gas in the vessel, we get the rate of change of the temperature of the gas; making a slight reduction we obtain the equation

$$\mathrm{d}T/\mathrm{d}\tau = e^{-E/R(T + T_0)}\, e^{-k(C/B)\tau} - (ax/B)T \qquad (1)$$

where $B = QAn_0V$ and $\tau = tB/C$; here t is measured from the moment the gas is admitted to the vessel, assuming that it warms up instantly to the temperature T_0, an assumption that will be discussed later. Since C as well as B is proportional to n_0, we may, for any given series of runs involving a definite substance and reaction vessel at a definite external temperature, T_0, but with varying pressure, consider τ to be a measure of the time from the start of the experiment expressed in a special set of units. Likewise the quantity B/ax, assuming that x is independent of the pressure, is a measure of the pressure used in a given experiment, and its value determines whether or not an explosion occurs in an experiment performed at a given temperature, T_0. In a case in which an explosion occurs integration of (1) will show that the temperature rises very suddenly after a lapse of time, and the time at which this sudden rise occurs may be set equal to the induction period,[4] while if explosion does not occur the temperature merely rises to a maximum and falls off again.

The differential equation (1) cannot be integrated analytically, but it may be solved numerically by the use of the Runge–Kutta formula.[5] In order to compare with the experimental data it is necessary to go through this process for different values of T_0 and ax/B. When this is done the value of τ at which the explosion occurs is known for any given conditions; this may be compared with the observed induction period t and B/C found. Now $B/C = QAn_0V/n_0VC_M = QA/C_M$ where C_M is the heat capacity per mole of azomethane; as A is known, we can calculate Q/C_M which should be practically constant for all experiments with a given composition of gas. If there are r moles of inert gas per mole of azo-

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[2] (a) Allen and O. K. Rice, THIS JOURNAL, **57**, 310 (1935); (b) Campbell and O. K. Rice, *ibid.*, **57**, 1044 (1935).

[3] Semenoff, *Z. Physik*, **48**, 571 (1928).

[4] The same principles have been used by Tizard and Pye [*Phil. Mag.*, **44**, 79 (1922)] in discussing the oxidation of certain hydrocarbons, but their experiments were of a different type than ours, and their equations cannot be used in treating the experiments of the type considered here.

[5] Scarborough, "Numerical Mathematical Analysis," The Johns Hopkins University Press, p. 273.

methane, then $C_M = C_A + rC_G$, where C_A is the molal heat capacity of azomethane and C_G that of the inert gas.

In order to take into account the correction factor $e^{-k(C/B)\tau}$, which allows for the amount of gas decomposed before explosion takes place, and which affects the induction period near the explosion limit and also changes the value of the critical explosion pressure somewhat, it is necessary to assume a preliminary value of C/B, which is precisely the quantity we are trying to obtain. One is thus required to make a series of successive approximations, a very long process on account of the tedious calculation involved in the use of the Runge–Kutta formula. This fact, together with the desirability of having an easy way to perform the integration for a considerable range of values of the constants involved, has led us to seek an approximate method of calculation. This will be presented in §2. It is first necessary, however, to carry out the more exact integration of Equation (1) for some special values of the constants involved, in order to gain some information about the general character of the solutions of (1) and to be able to verify the accuracy of the approximate method.

For this purpose we have taken among others the case where T_0 = 630°K. and $kC/B = 1.27 \times 10^{-21}$ and E = 51,200 calories per mole. These values were estimated to correspond roughly to the situation with azomethane at 630°K. Figure 1 shows the calculated T *vs.* τ curves for various values of ax/B. It is seen that, as expected, the curves are definitely of two classes, the curves for small values of ax/B (large values of the pressure) being such as one would expect to correspond to an explosion, while the curves for large values of ax/B correspond to a quiet decomposition in which the temperature reaches a relatively low maximum, and then drops off. In the case of the explosive curves, the theory does not predict an exact instant for the explosion to occur, but certainly fixes it within an interval of time much smaller than the experimental error in determining the induction period. The critical value of ax/B appears to lie between 2.86×10^{-19} and 2.87×10^{-19}. It is, however, not certain that this value can be determined as closely as indicated by these figures, for very close to the explosion limit the curves are very sensitive to slight inaccuracies in the calculation, and it is quite possible that one which appears to be explosive actually should not be, or *vice versa*. But if the curve is only so far from the explosion limit as the one for $ax/B = 2.84 \times 10^{-19}$ in Fig. 1, the critical τ for explosion is no longer sensitive to slight errors. For values of the pressure very near the explosion limit very large values of τ are theoretically possible, but experimentally these have not been realized. It is, in general, impossible to adjust the pressure closely enough to get within the critical range of pressures, and it is also probable that the theory fails in this region, as k is not actually constant as we have assumed.

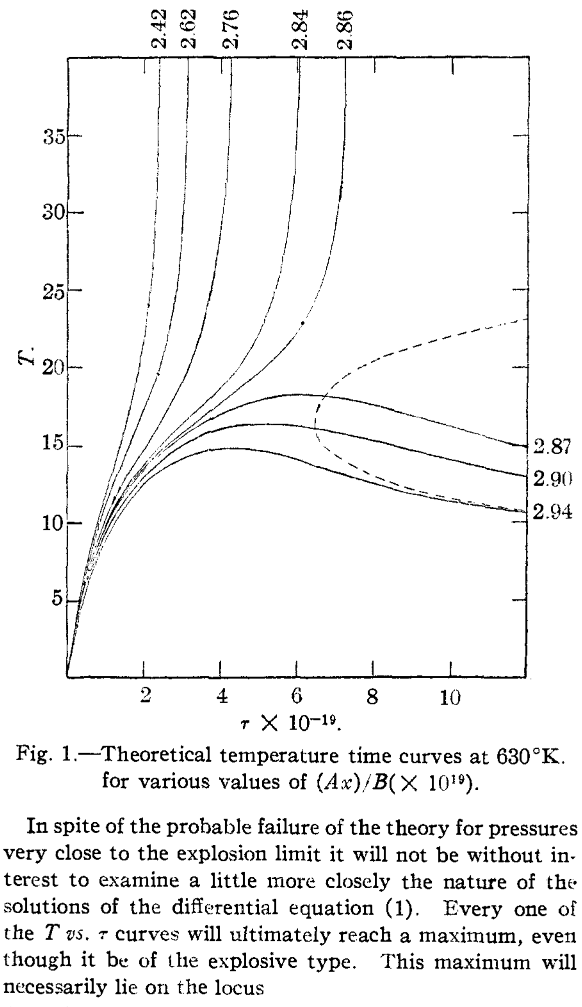

Fig. 1.—Theoretical temperature time curves at 630°K. for various values of $(Ax)/B(\times 10^{19})$.

In spite of the probable failure of the theory for pressures very close to the explosion limit it will not be without interest to examine a little more closely the nature of the solutions of the differential equation (1). Every one of the T *vs.* τ curves will ultimately reach a maximum, even though it be of the explosive type. This maximum will necessarily lie on the locus

$$(kC/B)\tau = -E/R(T + T_0) - \ln(ax/B) - \ln T \quad (2)$$

which makes $dT/d\tau$, as given by Equation (1), zero. The locus defined by Equation (2) for $ax/B = 2.86 \times 10^{-19}$ is shown (broken curve) in Fig. 1; the loci for other values of ax/B near this will be of just the same shape, but displaced along the τ axis a short distance. These loci are s-shaped, starting at $\tau = \infty$ for $T = 0$ and eventually reaching $\tau = -\infty$ for $T = \infty$. There are two points where the locus (2) has a vertical slope; one is shown, the other one is at a value of T approximately equal to

E/R, which is of the order of 25,000°, and a value of τ approximately $(B/kC)\ (E/RT_0 - 1 + 2\ \ln(RT_0/E))$, or about 32×10^{19}, greater than the value of τ for the first point of vertical slope. This value of τ gives the longest theoretically possible induction period. The explosive curves theoretically reach the upper branch of (2), that is, the part of the locus defined by (2) which is going out to $\tau = -\infty$; the values of T thus theoretically attained are greater than 25,000°. Such values will obviously not actually be reached, for one reason because k will not actually be independent of T and therefore the azomethane is used up before such temperatures are reached. The curves which have their maxima on the lower and middle branches of (2), up to the second point of vertical slope, where the locus defined by (2) turns around and heads toward $\tau = -\infty$, are the non-explosive curves. Theoretically there is a perfectly continuous transition between explosive type and non-explosive type curves, the transition occurring in an astonishingly small range of values of ax/B.

§2. Approximate Integration of Equation (1)

In order to get an approximate integration of Equation (1) we first see what can be done if the term $e^{-k(C/B)\tau}$ is set equal to 1. Under these circumstances we may, from Equation (1), write for τ_c, the critical value of τ at which explosion takes place

$$\tau_c = \int_0^{2RT_0^2/E} [e^{-E/R(T + T_0)} - (ax/B)T]^{-1}\,\mathrm{d}T \quad (3)$$

The upper limit in this integral is obtained in the following way. In the theory of Semenoff the rise in temperature at the explosion limit is equal approximately to[2a] RT_0^2/E, this being also very approximately the temperature at which the locus defined by Equation (2) has infinite slope, as shown in Fig. 1. From Fig. 1 it is obvious that, though τ_c cannot, as we have said, be exactly defined, it will be very reasonable to determine a value by integrating to the temperature where T is equal to twice the value RT_0^2/E.

If we make the allowable approximation[6] $(1 + T/T_0)^{-1} = 1 - T/T_0$ then we may write Equation (3) in the form

$$\tau_c = \int_0^{2RT_0^2/E} [e^{-E/RT_0}\,e^{ET/RT_0^2} - (ax/B)T]^{-1}\,\mathrm{d}T \quad (4)$$

If we set $y = ET/RT_0^2$ and $f = (ax/B)\ (RT_0^2/E)\ e^{E/RT_0 - 1}$ this takes the form

$$\tau_0 = (RT_0^2/E)e^{E/RT_0 - 1}\,I_0 \quad (5)$$

where

$$I_0 = \int_0^2 (e^{y - 1} - fy)^{-1}\,\mathrm{d}y \quad (6)$$

I_0 may be evaluated as a function of f from Equation (6) by numerical integration. By its definition, f is inversely proportional to P, the pressure, x being assumed independent of pressure.

Now the equation for the critical explosion pressure[7] is also based on the same approximations made so far in the considerations of this section. Using this equation we see that at the critical explosion pressure f is equal to 1 and we may set

$$f = P^*/P \quad (7)$$

where P^* is the critical explosion pressure of the approximate theory. For explosive runs, of course, $f < 1$.

Allowance for the term $e^{-k(C/B)\tau}$ of Equation (1) may be made in an approximate manner as follows. In the actual calculation of the curves in Fig. 1 one finds that the value of τ at which the curve begins to rise rapidly is largely determined by its behavior in the neighborhood of the inflection point, which occurs at a value of τ very near to $\tau_c/2$ and a value of T very near RT_0^2/E. This suggests that we replace the exponential term in question by a sort of average value, namely, $e^{-k^*(C/B)\tau_c/2}$, where k^* is the value of the rate constant at the temperature $T_0 + RT_0^2/E$. We then get in place of Equation (4), the equation

$$\tau_0 = \int_0^{2RT_0^2/E} [e^{-E/RT_0}\,e^{ET/RT_0^2}\,e^{-k^*(C/B)\tau_c/2} - (ax/B)T]^{-1}\,\mathrm{d}T \quad (8)$$

in which τ_c is involved inside the integral sign as well as on the left-hand side of the equation. This equation is to be solved for τ_c. It is convenient to define a quantity I, similar to the quantity I_0 of Equation (5) by the relation

$$\tau_0 = (RT_0^2/E)e^{E/RT_0 - 1}\,I \quad (9)$$

the difference between the value of τ_c obtained from Equation (8) and that given by Equation (4) being expressed by the difference between I and I_0. If we make the substitutions following Equation (4) and, further, set

$$\Theta = k^*(C/2B)(RT_0^2/E)e^{E/RT_0 - 1} \quad (10)$$

then it is readily seen from Equations (8) and (9) that

$$I = e^{\Theta I} \int_0^2 (e^{y - 1} - e^{\Theta I} fy)^{-1}\,\mathrm{d}y \quad (11)$$

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[6] We may note that under this approximation Equation (1) may be written in the form

$$\mathrm{d}y/\mathrm{d}J = e^{y - 1}\,e^{-\phi J} - fy$$

where

$$J = \tau(E/RT_0^2)e^{1 - E/RT_0}$$
$$\phi = k(C/B)(RT_0^2/E)e^{E/RT_0 - 1}$$

and y and f are defined just following Equation (4). This would make the Runge–Kutta calculations much easier, for the effects of T_0 and $k(C/B)$ are both taken care of essentially by the one parameter ϕ. This would greatly lessen the number of calculations needed, but they are still sufficiently laborious to make it seem worth while to develop the approximation method of this section.

[7] Ref. 2a, Equation (5).

Now the integral appearing in Equation (11) is simply the integral I_0 with the argument $fe^{\Theta I}$ appearing in place of f. We can thus write a functional equation connecting I and I_0

$$I(f) = e^{\Theta I(f)} I_0(fe^{\Theta I(f)}) \qquad (12)$$

in which the quantity in parentheses following an I or I_0 is the argument of which that I or I_0 is a function. This functional equation for I may be solved and I found as a function of f by the method presented in the Appendix. The results of these calculations for a number of different values of Θ are shown in Fig. 2. (The values given on the curves are 1760 Θ.)

Now the fact that the curves bend back indicates that for any given value of Θ there is a certain largest value of f above which there are no real solutions of the functional Equation (12). This suggests that this largest value of f corresponds to the corrected explosion limit. Equation (7) gives f in terms of P and P^*, the latter being the uncorrected critical pressure. If we wish to get I for any Θ as a function of P/P_1^* where P_1^* is the corrected critical pressure we can do this by noting that[8]

$$P/P_1^* = f_\Theta/f \qquad (13)$$

where f_Θ is the largest value of f for the given Θ. Thus, to get I as a function of P/P_1^* or f_Θ/f we simply move the curves of Fig. 2 to the left till the point of infinite slope touches the axis, $\log f = 0$. The result is shown in Fig. 3. The real justification of this procedure is that in special cases the curve obtained agrees with the result obtained by integrating Equation (1) directly, using the Runge–Kutta formula. This is shown in Fig. 3. The circles and triangles represent the values $\tau_c/(RT_0^2/E)e^{E/RT_0 - 1}$, where τ_c has been calculated by means of the Runge–Kutta formula from (1), and P/P_1^* has been set equal to the critical value of Ax/B divided by the value of Ax/B corresponding to the particular value of τ_c. It is seen that the agreement is very good, especially when one bears in mind that the Runge–Kutta method does not give the explosion limit very accurately, and that all points of a given set of calculations should be shifted horizontally by an amount corresponding to the error in the explosion limit. We may therefore use the the approximation developed in this section with some confidence, except very close to the explosion limit where all calculations break down. Since all our calculations do break down near the explosion limit it is not surprising that an attempt to go beyond the explosion limit results in the upper branches of the curves of Fig. 2, which can have no physical meaning.

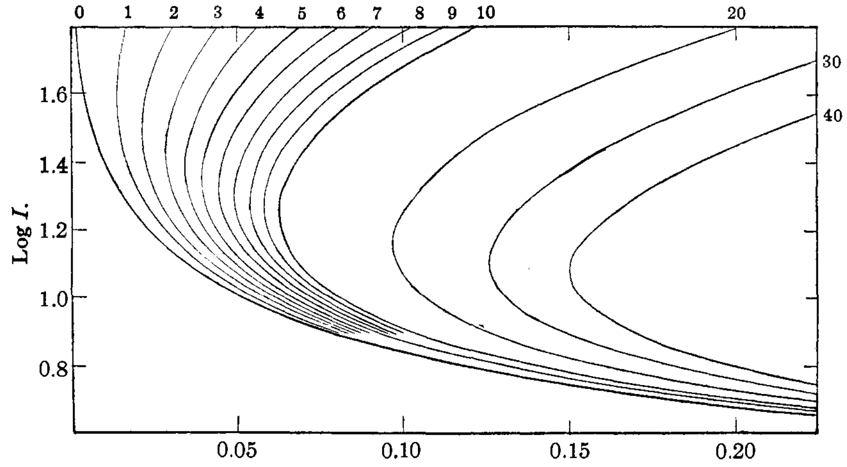

Fig. 2.

In an experiment we have a measurement of the time lag, which we may call t_c and which we may assume gives us $(C/B)\tau_c$. Furthermore, we know the ratio of the pressure to the critical pressure, which gives P_1^*/P. We also know T_0 and k^*. We therefore choose from among the curves of Fig. 3 that one which gives us the correct value of $(C/B)\tau_c = 2\Theta I/k^*$ (see Equations (9) and (10)) at the given value of P_1^*/P. We thus find the value of Θ corresponding to the particular experiment, and from this we can get Q/C_M, where C_M is the heat capacity of the reacting gas per mole of azomethane. This quantity is obtained from Θ by noting that $k^* = Ae^{-E/R(T_0 + RT_0^2/E)}$, which is approximately equal to $Ae^{1 - E/RT_0}$. Substituting this into Equation (10), and remembering the definitions of C and B we get

$$\Theta = (C_M/Q)(RT_0^2/2E) \qquad (14)$$

Since Q/C_M will not be expected to vary very much over the range of temperatures which can

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[8] Equation (13) can be used to correct the critical pressure given by the Semenoff theory. However, Equation (14) shows that Θ should be practically constant for any given explosive reaction over the range of temperatures in which it can be studied. The correction to $\log P^*$ is therefore essentially a constant independent of the temperature, and hence is of no practical importance. However, for purposes of notation, it is assumed hereafter in this paper that the experimental critical pressure gives a measure of P_1^*.

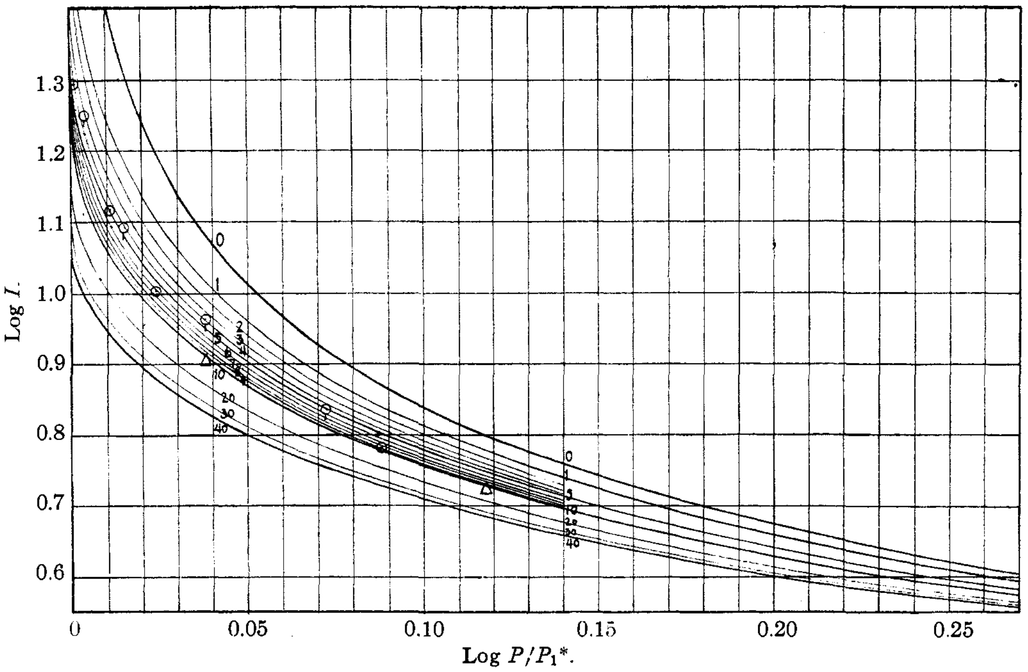

Fig. 3.—Data for Runge–Kutta points: ♀, E = 51,200, T_0 = 630°K., 1760 θ = 3.66; ○, E = 51,200, T_0 = 614°K., 1760 θ = 6.66. △, E = 41,500, T_0 = 553°K., 1760 θ = 7.82.

be studied, we should get the same value for all experiments with a given substance or mixture, and this will be a test of the theory

§3. The Heating of the Gas

In the above discussion we have neglected the time it takes to heat up the gas when it enters the reaction vessel. It is rather difficult to make an exact calculation of this quantity because the gas enters the reaction vessel through a hot tube where it receives a preheating, in what is probably a negligible length of time. If this heats the gas to a temperature equal to $T_0 - T'$, then the time (multiplied by B/C) for the gas to heat up to the wall temperature, T_0, is, from Equation (1) (which should hold for this process as it does for the heating up of the gas after the temperature T_0 has been reached)

$$\tau' = \int_{-T'}^{0} [e^{-E/R(T + T_0)} - (ax/B)T]^{-1}\,\mathrm{d}T \quad (15)$$

In this we have set the term $e^{-k(C/B)\tau}$ equal to 1, which is surely reasonable in this case. τ' determines the time which elapses before "zero time," that is before the time at which the gas is at the temperature T_0, and it is to be added to τ_c before comparing with the experiments. Making the same substitutions as were made to get τ_c in the form (5) we find

$$\tau' = (RT_0^2/E)e^{E/RT_0 - 1} I' \quad (16)$$

where

$$I' = \int_{-T'/T^*}^{0} (e^{y - 1} - fy)^{-1}\,\mathrm{d}y \quad (17)$$

where $T^* = RT_0^2/E$. We have evaluated I' for a number of values of f for $T'/T^* = 5$ and for $T'/T^* = 10$. These values are given in Table I together with values of I_0. It will be seen from this table that I' is not very sensitive to T'/T^* when the latter is as great as 5, and all our subsequent calculations have been carried out using this value.

Table I

Values of I_0 and I'

f	I_0	$I'(T'/T^* = 5)$	$I'(T'/T^* = 10)$
0.99	40.81	3.091	3.791
.98	27.22	...	...
.96	18.80	...	...
.95	....	3.184	3.914
.94	14.82	...	...
.90	10.89	3.317	4.087
.85	....	3.464	4.280
.80	7.04	...	...
.70	5.392	4.010	...
.50	3.819	5.152	...

§4. Comparison with Experiment

Tables II and III show all measurements of the induction period with azomethane and all of those made with ethyl azides No. 5 and No. 8,[9]

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[9] See the discussion by Campbell and Rice, Ref. 2b, of the various samples of azide used.

with the exception of some in which the temperature was uncertain. These runs are arranged in groups, all in any group having been done at the same time and at very approximately the same temperature, and the data for the highest pressure non-explosive run in each group are also given at the beginning of each group. These non-explosive runs are designated by the symbol ∞ in the "t_c, obs." column. In Table IV we give some examples illustrating the method by which Q/C_M is calculated from the observed time. The first row gives the absolute temperature; the second the logarithm of the ratio of the pressure P of the particular experiment to the critical explosion pressure $P_1{}^*$; the third row gives the observed induction period in seconds; the fourth row gives log A, which differs in different cases because of the falling off of the rate constant

TABLE II

INDUCTION PERIODS FOR AZOMETHANE EXPLOSIONS

Expt.	Temp., °C.	Press. (total), mm.	Ind. period, sec.
100% $(CH_3)_2N_2$ 200-cc. bulb			
255	341.0	189	∞
253	341.0	193	7.5
248	370.0	30	∞
247	370.4	31.5	2.0
244	358.3	54.5	∞
245	358.3	56.5	3.8
242	357.7	55.5	4.0
158	371.9	27	∞
157	371.9	29	2.2
156	371.5	32	1.4
153	346.8	101.5	∞
155	347.0	103	5.2
154	347.2	104.5	4.8
151	353.3	66	∞
150	353.3	68	5.5
147	386.5	17.5	∞
148	385.7	19	1.0
144	378.2	22	∞
146	378.5	23	1.4
145	378.5	24.5	1.2
141	363.5	37.5	∞
142	363.4	38.5	4.0
140	363.6	41	3.1
100% $(CH_3)_2N_2$ 50-cc. bulb			
265	353.0	149	∞
263	353.5	152	3.2
261	355.3	132	∞
260	355.0	137.5	3.4
50.7% $(CH_3)_2N_2$, 49.3% N_2 200-cc. bulb			
287	374.8	44.5	∞
286	375.1	45.5	4.1
285	375.2	49	2.0
284	374.8	53	2.0
279	361.3	90	∞
283	361.0	91	4.1
282	361.4	93	3.6
281	361.3	95	3.6
32.5% He, 67.5% $(CH_3)_2N_2$ 200-cc. bulb			
180	376.8	38	∞
179	376.8	38.5	2.0
177	377.0	41.5	<1.0
176	377.3	44	<1.0
186	352.0	139	∞
185	352.0	141	4.5
172	352.0	144	3.0
171	352.0	147.5	3.0
170	352.0	150	2.6
169	352.0	153	2.6
174	363.7	69	∞
175	363.7	71.5	4.2
173	363.9	77	2.0
59.2% He, 40.8% $(CH_3)_2N_2$ 200-cc. bulb			
221	377.2	75.5	∞
223	377.2	77	2.0
222	377.0	79	1.8
218	372.0	99	∞
217	372.0	101.5	3.0
213	367.9	121	∞
215	367.9	122	3.0
214	368.3	123.5	2.0
212	367.9	126.5	2.4
210	359.2	166.5	∞
209	359.4	168	4.0
207	359.5	172	3.0
206	359.4	181	2.8
205	356.9	209	∞
203	356.9	210	4.4
202	356.7	219.5	3.2
201	356.8	231	3.0
200	349.9	296.5	∞
199	351.3	307	4.0
190	372.0	90	∞
192	372.3	95.0	1.4
191	371.7	99.5	1.4
187	359.5	214	2.0
76.3% He, 23.7% $(CH_3)_2N_2$ 200-cc. bulb			
241	338.7	143	∞
240	339.0	144	2.0
234	369.4	220.5	∞
231	369.5	221.5	3.2
235	369.3	223	3.0
230	361.8	322	∞
229	362.0	323	5.0
228	362.0	328.5	3.8
226	361.8	336	3.2
225	361.8	357	2.4
224	362.0	377.5	2.2

The apparently anomalous value of t_c for Expt. 217 as compared with Expts. 191 and 192 is due to the former having been performed with a different preparation (probably slightly impure) which gave a higher explosion limit than the preparation used in the latter two experiments.

TABLE III

INDUCTION PERIODS FOR ETHYL AZIDE EXPLOSIONS

Expt.	Temp., °C.	Press. (total), mm.	Ind. period, sec.
8th Azide 50-cc. bulb			
428	265.5	108.7	∞
429	265.0	111.0	4
401	269.8	73.2	∞
402	270.0	74.2	4
400	269.8	74.5	4
399	270.0	75.1	2
423	274.2	50.9	∞
425	274.3	51.8	4
408	279.7	34.1	∞
406	280.0	35.5	1.5
411	290.1	17.9	∞
412	290.0	18.9	2
416	300.3	9.6	∞
414	300.4	11.7	0.5
413	300.1	15.1	.5
8th Azide 200-cc. bulb			
336	258.5	104.7	∞
337	258.6	105.7	6
335	258.6	107.0	5
330	259.8	90.4	∞
332	260.0	92.9	5
331	259.9	94.0	4.5
444	260	85.0	∞
443	260	86.1	5
442	260	86.9	5
324	262.8	64.4	∞
325	262.1	72.0	6
323	263.1	63.5	∞
322	263.0	65.7	4.5
320	265.0	51.8	∞
319	265.0	53.3	5
318	264.7	54.0	5
317	264.9	54.5	4
316	265.0	55.2	4
315	265.2	55.2	3.5
314	265.0	55.5	3.5
201	265.1	58.5	∞
202	265.3	59.6	3
206	265.1	55.5	∞
204	265.4	56.3	4
203	265.0	58.0	3.5
195	265.0	54.5	∞
194	265.0	55.5	5
191	270.0	36.0	∞
192	270.1	36.8	4.5
189	270.2	34.6	∞
188	270.4	35.2	3.5
187	270.0	36.9	3
380	270.0	32.3	∞
379	270.0	34.2	4
378	270.0	37.0	3
208	274.5	24.7	∞
207	274.5	25.5	3.5
383	280.0	15.3	∞
382	280.0	16.5	2
365	300.0	5.0	∞
364	299.8	6.2	1
5th Azide 200-cc. bulb			
102	269.5	36.8	∞
103	270.0	38.8	4
130	269.7	36.7	∞
129	270.1	36.4	4.5
118	279.6	17.3	∞
117	280.0	17.4	3
101	280.0	15.0	∞
100	280.0	16.8	3
122	289.8	9.5	∞
120	289.8	10.4	2
123	290.0	10.4	1.5
50.1% 5th Azide, 49.9% CO_2 200-cc. bulb			
107	269.9	73.0	∞
106	269.8	73.8	3
115	280.0	34.9	∞
116	280.0	36.0	3
126	289.9	19.0	∞
125	289.7	19.8	2.5
124	289.8	19.8	1.5
49.9% 8th Azide, 50.1% He 200-cc. bulb			
241	270.4	103.0	∞
240	270.7	103.5	3
247	279.9	49.8	∞
248	280.0	52.7	1.5
251	284.9	37.0	∞
250	285.3	38.6	1.5
253	289.9	28.5	∞
252	289.9	29.0	1
258	300.0	21.4	∞
256	299.8	22.7	0.5
255	299.3	23.0	.5
254	300.0	24.6	.5
66.3% 8th Azide, 33.7% He 200-cc. bulb			
265	270.0	67.7	∞
264	270.0	68.8	3
266	274.2	48.7	∞
267	274.9	47.0	3.5
268	280.1	31.0	∞
270	280.2	32.0	3
271	285.0	23.7	∞
272	285.0	25.0	2
276a	295.2	12.8	∞
276	295.3	13.8	1.5
283	305.6	8.3	∞
280	305.7	11.0	1

with pressure; the fifth row gives the value[9a] of k^*; the sixth row gives trial values of $17.6\ \Theta$; from these are calculated I and I', which are given in rows seven and nine; to get I' requires also the value of f, given in row eight, which is obtained from the values of P/P_1^* and Θ by use of Equation (13) and Fig. 2; in the tenth row are given the calculated values for

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[9a] This quantity was calculated using 40,000 as the activation energy for ethyl azide; this was not the final best value, but a corresponding value of A was used, and the error thus made was small. For azomethane the activation energy is 51,200.

TABLE IV

CALCULATIONS OF Q/C_M FOR EXPTS. 156 AND 187 OF TABLE II AND 316 OF TABLE III

T_0	644.5	632.5	538.0
Log (P/P_1^*)	0.048	0.106	0.020
t_c (obs.)	1.4	2.0	4.0
Log A	15.85	15.95	13.915
k^*	0.083	0.049	0.0313
17.6 Θ	.09–0.10	.09–0.10	.08–0.09
I	7.60–7.50	5.61–5.56	10.22–10.02
$-\log f$	0.107–0.111	0.165–0.169	0.074–0.079
I'	3.69–3.71	4.08–4.11	3.49–3.52
t_c (calcd.)	1.39–1.54	2.02–2.24	3.98–4.43
17.6 Θ expt.	0.091	0.089	0.080
Q/C_M	1560	1530	1580

TABLE V

CALCULATION OF Q/C_M AND Q

Expt.	T_0, °K.	Log P/P_1^*	Log A	t_c, obsd., sec.	Q/C_M	C_M cal./mole deg.	Q cal./mole
			100% $(CH_3)_2N_2$				
156	644.5	0.048	15.85	1.4	1560	25.7	40000
145	651.5	.041	15.82	1.2	1410		36200
140	636.6	.028	15.88	3.1	1170		30000
			67.5% $(CH_3)_2N_2$, 32.5% He				
173	636.9	0.040	15.91	2.0	1570	27.1	42500
171	625.0	.023	15.96	3.0	2230		60500
170	625.0	.030	15.96	2.6	2450		66400
169	625.0	.038	15.96	2.6	2310		62600
177	650.0	.035	15.83	1.0	1780		48200
			40.8% $(CH_3)_2N_2$, 59.2% He				
191	644.7	0.032	15.88	1.4	1560	30.0	46800
201	629.8	.042	15.95	3.0	1450		43500
202	629.7	.020	15.95	3.2	1590		47700
206	632.4	.034	15.93	2.8	1430		42900
187	632.5	.106	15.95	2.0	1530		45900
212	640.9	.017	15.91	2.4	1180		35400
222	650.0	.015	15.86	1.8	1020		30600
			23.7% $(CH_3)_2N_2$, 76.3% He				
224	635.0	0.068	15.95	2.2	1280	35.3	45200
225	634.8	.044	15.94	2.4	1350		47700
226	634.8	.018	15.94	3.2	1190		42000
			50.7% $(CH_3)_2N_2$, 49.3% N_2				
281	634.3	0.021	15.91	3.6	1130	30.5	34500
284	647.8	.071	15.84	2.0	830		25300
285	648.2	.037	15.83	2.0	940		28700
			100% $C_2H_5N_3$ No. 8				
314	538.0	0.023	13.915	3.5	1790	25.3	45300
316	538.0	.020	13.915	4.0	1580		40000
378	543.0	.044	13.900	3.0	1340		33900
315	538.3	.021	13.915	3.5	1800		45500
413	573.2	.150	13.857	0.5	1200		30400
			49.9% $C_2H_5N_3$ No. 8, 50.1% He				
255	572.4	0.018	13.842	0.5	1970	28.3	55700
254	573.1	.047	13.846	.5	1500		42500

the induction period, obtained from the formula $t_c = 2\Theta(I + I')/k^*$; from these we obtain by comparison with the observed value of t_c and by interpolation the experimental value of 17.6 Θ, and this enables us to calculate Q/C_M from Equation (14). Table IV shows the order of magnitude of the various quantities involved. The first run presented is an extreme case as regards the relative importance of I' and I. In all others, I is considerably larger than I', the other examples given being typical.

In Table V we give in condensed form the results of all calculations of Q/C_M. This table covers all experiments given in Tables II and III in which the pressure was more than 1.04 times the critical pressure. In most cases the critical pressure used was simply the average of the pressures of the highest non-explosive and the lowest explosive runs of the particular group of experiments to which the run belonged, all runs having been made primarily to determine the explosion limits; but in the case of pure azomethane it was considered more accurate (on account of temperature fluctuations in a given series) to draw a smooth curve through the values of P_1^* plotted as a function of T and then to read P_1^* from the curve.

In order to get Q we have made an attempt to estimate roughly the specific heats of azomethane and ethyl azide. Though the Raman spectra of these substances have apparently not been obtained, we may nevertheless assign approximate frequencies to each of the bonds or modes of vibration in these molecules, on the basis of the Raman spectra of similar compounds.[10] These can then be translated into contributions to the specific heat. Table VI gives the results. The degeneracy values in the second column were obtained from simple geometrical considerations. The azide radical was assumed to be linear. The frequencies in the third column are estimated, following Kohlrausch. The N=N frequencies in both azomethane and ethyl azide are assumed equal to the C=O frequency in ketones. The "skeleton bending" frequencies are merely a very rough guess; but their values are undoubtedly lower than the other frequencies, and since at the temperatures used such low frequencies are nearly fully excited, their exact value does not matter much. Contributions to C_v (fourth column) are calculated for each vibrational de-

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[10] Kohlrausch, "Der Smekal-Raman Effekt," Verlag Julius Springer, Berlin, 1931, especially pp. 154, 157, 206, 314; *Z. Elektrochem.*, **40**, 429 (1934).

gree of freedom by the formula $C_v = R(h\nu)^2 e^{h\nu/kT}/(kT)^2 (1-e^{h\nu/kT})^2$, with T taken as 620°K. for azomethane and 550°K. for ethyl azide. The result can lay no great claim to accuracy; we should expect, however, that its probable percentage error is no greater than that of our determination of Q/C_M. In view of the other uncertainties involved we have not thought it worth while to consider the change of specific heat with temperature for the small temperature range available.

TABLE VI

CALCULATION OF SPECIFIC HEATS

Degree of freedom	Degeneracy	ν, cm.$^{-1}$	C_v, cal. per mole
	Azomethane		
Translation	3		2.98
Rotation	5		4.96
C—H stretching	6	2940	0.62
C—N stretching	2	1035	2.52
N=N stretching	1	1714	0.62
C—H bending	10	1430	8.94
Skeleton bending	3	600	5.10
	Total C_v for azomethane =		25.7
	Ethyl azide		
Translation	3		2.98
Rotation	5		4.96
C—N stretching	1	900	1.28
C—C stretching	1	1050	1.08
N=N stretching	2	1800	0.81
C—H stretching	5	2940	.27
C—H bending	7	1430	4.87
C—H bending	2	1200	1.83
Skeleton bending	4	400	7.23
	Total C_v for ethyl azide =		25.3

Using these values of C_v, we have calculated Q for azomethane and ethyl azide. For the mixtures the formula of §1 for C_M is used, C_G being taken as 3.0 cal. per mole for helium, and 4.9 for nitrogen.[11] The results are given in the last column of Table V.

Over the temperature range for which it is possible to make measurements Q should be approximately constant. It will be seen that the values actually obtained vary considerably, but in view of the considerable errors necessarily involved the variation does not seem excessive. Errors may occur in the actual measurement of the induction period, which is very short, and may also be due to slight changes in temperature during a series of runs, which causes the explosion limit to be determined for a slightly different temperature than that at which the given run was made. Any error in the explosion limit due to this or any other cause produces a relatively large error in Q. But perhaps the greatest source of error is the finite time which is required for the gas to enter the reaction vessel. This was especially great in the case of ethyl azide, as noted in the preceding paper,[2b] and the pressure in the reaction bulb had not, in general, become quite equalized with the storage bulb before the stopcock was closed. However, since the largest portion of the gas undoubtedly rushes in almost immediately, and since in almost all cases the stopcock can be closed before the explosion occurs, we believe that the results are of significance even though considerable error can no doubt be caused, and the effect should be partly neutralized by the fact that the same error enters into the determination of the explosion limit. In general, the variations in Q seem to be quite random, the only apparent exception being the values of Q for azomethane in the presence of nitrogen. It is impossible to say whether this variation, for which no obvious explanation is available, is real or not.

The final average values of Q are 43,000 calories per mole for azomethane and 42,000 for ethyl azide. It is possible that these values not only are subject to the errors inherent in the experiments, but also contain systematic errors due to the assumptions made in the theory, particularly the assumption that the rate at which heat is removed from the vessel is simply proportional to the difference in temperature between the gas and the wall of the vessel. However, since the proportionality constant in this expression does not enter into the final results at all, it seems likely that the result will not be very sensitive to the form of the expression, either. We believe that the values of Q given are probably correct to within about 10,000 calories per mole.

§5. The Attainment of Temperature Equilibrium in a Reaction which Is Not Exothermic

When the rate of an ordinary non-explosive reaction is measured, the gas is admitted to a heated reaction vessel at a certain time, and it is assumed that the time required to heat it to the temperature of the vessel is negligible. The considerations of the present paper give us the possibility of discussing this assumption; we can learn something about heat transfer in non-explosive gases, whose decompositions are slightly exothermic or endothermic (or which do not react at all) by in

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(11) "International Critical Tables."

ference from the properties of the explosive gases as deduced in the preceding sections of this paper.

The results of the last section show that the length of time required to heat the gas up to the temperature of the vessel is generally only a fairly small fraction of the entire induction period. This is due in part to the fact that, as the temperature of the vessel is approached, the gas begins to decompose, giving out heat and warming itself up. If the reactions were not so exothermic it would take considerably longer for the final temperature adjustment to occur, and if it were endothermic the situation would be even less favorable. In the case in which the reaction neither gives out nor absorbs heat, the rate of increase of temperature is given by Equation (1) with the first term on the right-hand left out, and, using t instead of τ, we see that the time required to heat up the gas from a temperature $T_0 - T'$ to a temperature, $T_0 - T''$, say, is given by

$$t = -\int_{-T'}^{-T''} \frac{C}{ax}\frac{\mathrm{d}T}{T} = \frac{C}{ax}\ln T'/T'' \qquad (18)$$

If we could determine x it would thus be possible to find how long it takes for a gas to heat up to within, say, 1° of the temperature T_0 from a temperature, say, 100° below. Now x can be determined for the explosive gases from the value of f, and we may reasonably assume that it is the same order of magnitude for all gases. From the definitions of f (following Equation (4)) and B, we have

$$\frac{ax}{Qn_0} = VA\,\frac{E}{RT_0^2}\,e^{1-E/RT_0}f = \frac{VEk^*}{RT_0^2}f \qquad (19)$$

Remembering that $C = C_{\mathrm{M}}n_0\,V$ we have

$$\frac{ax}{C} = \frac{Q}{C_{\mathrm{M}}}\frac{Ek^*}{RT_0^2}f \qquad (20)$$

Taking, for example, the data from the first run in Table IV we get $ax/C = 6.3$ sec.$^{-1}$, while if $T'/T'' = 100$ then t from Equation (18) is equal to about 0.7 second. In this case the total pressure is about 32 mm. and the experiment was done with a 200-cc. flask. Since C is proportional to n_0 and V it is seen that this time would be increased at higher pressures and with larger vessels. The matter is somewhat complicated by the fact that the results of our previous work[2] indicate that x is not a true constant, but it is fairly obvious that with pressures up to an atmosphere and with conditions under which reaction rates are usually run, the gas will come to nearly the temperature of the flask within at most half a minute. It may be well to note that this is far faster than equilibrium could be established by heat conduction alone, and convection must play an important role in the mechanism of heat transfer.

In the case of a non-explosive run of a gas which does react exothermally, the time necessary to reach what is essentially a steady state temperature should require a length of time of the order of magnitude of the induction period in an explosive run. According to the simple Semenoff theory the temperature rise T should never reach a value greater than $T^* \cong RT_0^2/E$ in a non-explosive run. An examination of Fig. 1 shows that actually in a run near the explosion limit the temperature surges up above that value and then drops back again. Excepting for a run exceedingly close to the explosion limit we may judge from Fig. 1 that all this will take place in a time not more than two or three times that occupied by the actually observable induction periods. Since this time is, in general, small compared to the half life of the decomposing substance, the calculation made in §5 of the paper of Allen and Rice[2a] should be valid in almost all cases.

Appendix

The solution of the functional equation (12) may be obtained by a series of successive approximations in the following manner. We define a quantity f' by the equation

$$f = f'e^{-\Theta I_0(f')} \qquad \text{(A)}$$

and take as a first approximation to $I(f)$ the quantity $I_1(f)$ defined by

$$I_1(f) = e^{\Theta I_0(f')}\,I_0(f') \qquad \text{(B)}$$

We then insert this quantity $I_1(f)$ into the right-hand side of Equation (12) in place of $I(f)$ to get a second approximation

$$I_2(f) = e^{\Theta I_1(f)}\,I_0(fe^{\Theta I_1(f)}) \qquad \text{(C)}$$

We now insert $I_2(f)$ into the right-hand side of Equation (12) and continue the process, getting finally for the nth approximation

$$I_n(f) = e^{\Theta I_{n-1}(f)}\,I_0(fe^{\Theta I_{n-1}(f)}) \qquad \text{(D)}$$

If the process converges, that is, if $I_n(f)$ approaches a limit as n becomes large, then it is easily seen that the limiting value of $I_n(f)$ satisfies Equation (12) and may thus be identified with $I(f)$. That the process does converge readily appears when one attempts to carry it out; in fact, I_1 is a sufficiently good approximation for our purposes and has been used in Fig. 2. The easiest way to get I_1 as a function of f is to start with given values of f' and Θ. Equation (A) then determines a value of f and Equation (B) gives the corresponding value of I_1; together they give a point on the curve for the given value of Θ.

Summary

When the differential equation connecting temperature with time in an exothermic gas reaction is integrated, a sudden temperature rise, corresponding to an explosion, is found to be indicated above a certain sharply defined pressure. From curves of this type, an approximate method for calculating the induction period in thermal explosions has been obtained, and has been applied to the explosions of azomethane and ethyl azide. Rough values of the heats of decomposition of these compounds are thereby obtained. A discussion is given of the rate at which a gas not reacting exothermically comes into thermal equilibrium when admitted to a heated vessel.

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Hydrogenation of Carbon Dioxide and a Correction of the Reported Synthesis of Urethans

BY MARK W. FARLOW AND HOMER ADKINS

In an attempt to prepare N-pentamethylene salicylamide through the reaction of methyl salicylate and piperidine at 250° under hydrogen, Wojcik and Adkins[1] obtained a product which they reported as phenyl N-pentamethylene urethan, *i. e.*, $C_6H_5OC(O)NC_5H_{10}$. They suggested that the supposed urethan might be formed through the decarboxylation of salicylic acid followed by the reaction of phenol, carbon dioxide and piperidine. They apparently confirmed this hypothesis by obtaining the same product from phenol, carbon dioxide and piperidine as from methyl salicylate and piperidine. A further study of the postulated reaction has shown that the alleged urethan was a mixture of phenol and formylpiperidine, $C_5H_{10}NC(O)H$. An equimolecular mixture of these two compounds has a constant and narrow boiling range about 10° higher than either component and shows an analysis for nitrogen very nearly the same as for the urethan. Similarly, the products reported as phenyl N-*n*-amyl and *n*-butyl-N-pentamethylene urethans have been found to be mixtures of formyl amines with phenol or butanol-1.

The identification and isolation of formylamines from the reaction products of hydrogen, carbon dioxide, amines and alcohols led to a study of the hydrogenation of carbon dioxide. The significant numerical results are given in the table and may be summarized as follows.

The hydrogenation of carbon dioxide to formic acid in the presence of an amine takes place at 80° or less over Raney nickel.

$$CO_2 + H_2 \longrightarrow HCO_2H$$
$$HCO_2H + RNH_2 \longrightarrow HCO_2NH_3R$$

For example, after one hour at 80° 1-Ph-2-aminopropanol-1 was converted to the formate in a yield of 55% based upon the amine, the carbon dioxide and hydrogen being in excess. The rate and temperature necessary for hydrogenation apparently varies with the structure of the amine as well as with the catalyst. At a sufficiently high temperature (250°) sheet brass, such as has been used in this Laboratory for fabricating liners for steel reaction vessels, is an active catalyst for the hydrogenation. If the hydrogenation is carried out at a temperature much above 100° in the presence of a primary or secondary amine, the formate is dehydrated and the amide (formylamine) is obtained.

$$HCO_2NH_3R \longrightarrow HC(O)NHR + H_2O$$

Since a variety of substances may be present under the conditions used for the hydrogenation, it is not possible to formulate with certainty the course of the reaction. Carbon dioxide might react with a primary or secondary amine with the formation of a carbamate

$$2R_2NH + CO_2 \longrightarrow R_2NC(O)ONH_2R_2$$

or since traces of water are present a carbonate might be formed

$$R_2NH + CO_2 + H_2O \longrightarrow (R_2NH_2)_2O_2CO$$

Dehydration of the carbonate would give the

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[1] Wojcik and Adkins, THIS JOURNAL, **56**, 2461 (1934).